

U.S. PATENT APPLICATION

OF

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FOR

METHODS TO CONTROL AND/OR PREDICT
RHEOLOGICAL PROPERTIES

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METHODS TO CONTROL AND/OR PREDICT RHEOLOGICAL PROPERTIES

This application claims the benefit under 35 U.S.C. §119(e) of prior U.S. Provisional Patent Application Nos. 60/459,230 filed April 1, 2003, 60/485,964 filed July 10, 2003, 60/485,965 filed July 10, 2003, and 60/491,632 filed July 31, 2003, which are all incorporated in its entirety by reference herein.

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a method for predicting the rheological properties of compositions comprising a filler in a matrix. The present invention further relates to a method of choosing a filler for a composition in order to achieve a desired rheological property.

[0002] In polymer or solvent-based compositions, other components may be added which contribute to the composition's ultimate properties. For instance, with respect to a polymeric composition, such as polyurethane, a filler or other particle is often present. However, in the past, typically the choice of a filler for a composition is not as elementary as simply picking any filler and adding it to the composition. In fact, it is known in the industry that each filler performs differently with respect to, for example, rheological properties. Thus, and strictly as an example, carbon black can be used as a filler, and it has been shown that one type of carbon black having certain properties such as a particular BET surface area, a DBP, tint strength, and the like can impart desirable rheological properties to a polymer composition while another carbon black having the same or similar physical parameters will not impart the same desirable rheological properties. Due to this phenomenon, in the industry, it was quite common to use past experiences in an effort to determine what filler would best interact with the components of a composition. However, even this strategy does not often work since, for example, various polymer compositions can differ from past polymer compositions, which results in the filler not providing the same desirable rheological properties.

[0003] Thus, it was quite common in the industry to simply use a hit and miss strategy wherein a carbon black or other filler is tested in a composition and then compared with another filler that is tested in the same composition until the desired rheological properties are achieved. This hit and miss strategy is quite costly, takes large blocks of time, and further does not result in the best filler being used to provide the most optimized rheological properties in the particular composition.

[0004] Thus, there is a need in the industry to provide a means to determine the best class of fillers for a particular composition in order to achieve the most optimized rheological properties for the composition.

SUMMARY OF THE PRESENT INVENTION

[0005] A feature of the present invention is to provide a means to choose fillers that will provide the most optimized rheological properties in a composition.

[0006] Another feature of the present invention is to provide a method to predict the rheological properties of a composition based on the use of a particular filler.

[0007] A further feature of the present invention is to provide filler-matrix combinations which provide desirable rheological properties depending on the use of the composition.

[0008] An additional feature of the present invention is to provide a means to change the rheology of a matrix by controlling the particular filler used.

[0009] Additional features and advantages of the present invention will be set forth in part in the description that follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the description and appended claims.

[0010] To achieve these and other advantages, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to a method for determining a rheological master curve for a composition comprising a filler in a matrix. The method comprises the steps of:

- a) determining the work of adhesion of the matrix to the filler;
- b) determining the work of cohesion of the filler;
- c) determining the difference between the work of cohesion and the work of adhesion;
- d) measuring a rheological property of the composition; and
- e) correlating the rheological property to the difference between the work of cohesion and the work of adhesion.

The works of adhesion and cohesion are preferably determined by measuring contact angle(s) or related properties (such as wicking rates) of a filler based on one or more probe fluids. The method can be repeated any number of times with different fillers, loading levels, and the like in order to determine the best filler for the polymer matrix.

[0011] The present invention further relates to a rheological master curve for a composition comprising a filler in a matrix, wherein the master curve correlates i) the difference between the work of cohesion of the filler and the work of adhesion of the matrix to the filler; and ii) a rheological property of the composition. This rheological master curve can be created for a variety of fillers (depending on morphology, loading levels and the like) based on the present invention.

[0012] The present invention further relates to a method of predicting a value for a rheological property of a composition comprising a filler in a matrix. The method comprises the steps of:

- a) determining the work of adhesion of the matrix to the filler;
- b) determining the work of cohesion of the filler;
- c) determining the difference between the work of cohesion and the work of adhesion; and
- d) correlating the difference between the work of cohesion and the work of adhesion to the value for the rheological property using the rheological master curve described herein.

[0013] The present invention further relates to a method of choosing a filler to achieve a desired value of a rheological property of a composition comprising the filler in a matrix. The method comprises the steps of:

- a) determining the surface energy components of several probe fillers;
- b) measuring the rheological property of a composition comprising one probe filler and the matrix;
- c) correlating the rheological property of the composition comprising the probe filler and the matrix to a difference between the work of cohesion of the probe filler and the work of adhesion of the matrix to the probe filler using the rheological master curve described herein;
- d) repeating steps b) and c) for each probe filler;

- e) calculating the surface energy components of the matrix from the correlated differences of step c) and the surface energy components of the probe fillers of step a);
- f) correlating the desired value of the rheological property of the composition comprising the filler in the matrix to a difference between the work of cohesion of the filler and the work of adhesion of the matrix to the filler using the rheological master curve described herein;
- g) choosing the target filler having the surface energy components which, when used to calculate the work of cohesion of the target filler and the work of adhesion of the matrix to the target filler, gives a difference which is similar to the correlated difference of step f).

[0014] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide a further explanation of the present invention, as claimed.

[0015] The accompanying drawings, which are incorporated in and constitute a part of this application, illustrate various aspects of the present invention and together with the description serve to explain the principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1 is a graph plotting shear rate versus shear stress for determining yield.

[0017] Figure 2 is a master curve showing the general correlation of work of cohesion minus work of adhesion and yield point.

[0018] Figure 3 is a master curve illustrating ranges of work of cohesion minus work of adhesion for a particular yield point.

[0019] Figure 4 is a master curve relating the difference between the work of cohesion work of adhesion for a single fluid.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0020] The present invention relates to a method to predict the rheological properties of a composition comprising a matrix and one or more fillers. In a preferred embodiment of the present invention, the method of predicting or determining the rheological properties of the

composition is based on determining the contact angle of the filler based on one or more probe liquids. Preferably, the contact angle of the filler is based on at least three different probe liquids. The surface energy components of the filler are then determined based on the measured contact angles. The method further involves measuring the contact angle(s) of the matrix (in a fluid state) based on at least one solid. Various conditions, such as increasing temperature, may be needed in order to attain the fluid state for the matrix. Preferably, the contact angle is determined from the contact angle of the matrix based on three different solids. The surface energy components of the matrix are then determined based on the measured contact angle(s). Then, the work of adhesion and the work of cohesion are determined as well as the difference between the work of cohesion and work of adhesion. This data by itself can predict the yield point of the composition by correlating this data to a master curve or formula.

[0021] In the present invention, the composition comprises at least one filler in a matrix. For purposes of discussion, the term “filler” has been used but it is understood to mean particles such as carbon black particles and the like. Any filler can be used in the present application such as, but not limited to, carbon products such as carbon black, silica (fumed or precipitated), kaolin, talc, mica, glass beads and the like and combinations thereof.

[0022] With respect to the matrix of the composition, any matrix can be used. For example, the matrix may be a polymer or polymeric material, a solvent-resin system, or a solvent. When the matrix is a polymer or solvent-resin system, the polymer or resin can be a thermoplastic or thermoset polymer. Specific examples include, but are not limited to, polyurethane, polyacrylates, polymethacrylates, epoxies, and the like. Further, the polymer or resin can be a homopolymer, copolymer, terpolymer, and/or a polymer containing any number of different repeating units, and can be any type of polymer, such as a random polymer, alternating polymer, graft polymer, block polymer, star-like polymer, and/or comb-like polymer. The polymer or resin can also be one or more polyblends, an interpenetrating polymer network (IPN); simultaneous interpenetrating polymer network (SIN); or interpenetrating elastomeric network (IEN).

[0023] Specific examples of polymers or resins include, but are not limited to, linear-high polymers such as polyethylene, poly(vinylchloride), polyisobutylene, polystyrene, polycaprolactam (nylon), polyisoprene, and the like. Other general classes of

polymers of the present invention are polyamides, polycarbonates, polyelectrolytes, polyesters, polyethers, (polyhydroxy)benzenes, polyimides, polymers containing sulfur (such as polysulfides, (polyphenylene) sulfide, and polysulfones), polyolefins, polymethylbenzenes, polystyrene and styrene copolymers (ABS included), acetal polymers, acrylic polymers, acrylonitrile polymers and copolymers, polyolefins containing halogen (such as polyvinyl chloride and polyvinylidene chloride), fluoropolymers, ionomeric polymers, polymers containing ketone group(s), liquid crystal polymers, polyamide-imides, polymers containing olefinic double bond(s) (such as polybutadiene, polydicyclopentadiene), polyolefin copolymers, polyphenylene oxides, poly(vinyl alcohols), polyurethanes, thermoplastic elastomers, and the like.

[0024] Generally, the polymers described in Volume 18 of the Encyclopedia of Chemical Technology, KIRK-OTHMER, (1982), page 328 to page 887, and Modern Plastics Encyclopedia '98, pages B-3 to B-210, and "Polymers: Structure and Properties," by C. A. Daniels, Technomic Publishing Co., Lancaster, Pa. (1989), all incorporated in their entirety herein by reference, can be used as the matrix for the compositions of the present invention. These polymers can be prepared in a number of ways and such ways are known to those skilled in the art. The above referenced KIRK-OTHMER section, Modern Plastics Encyclopedia, and C. A. Daniels' reference provide methods in which these polymers can be prepared.

[0025] With respect to determining the contact angle of the filler based on one or more probe liquids, the probe liquids can be any liquid. Preferably at least three probe liquids are used and these probe liquids are different from each other. Preferably the probe liquids are different from each other with respect to surface tension. For example, various properties of various probe liquids are identified in the example section which can be used in the present invention and include, but are not limited to, pentane, water, formamide, ethylene glycol, and the like.

[0026] The contact angle of the filler based on these probe liquids can be determined in any acceptable manner. For instance, and preferably, the filler is placed in a container such as a cell wherein the filler is packed into the cell. Preferably, the cell constant of the packed powder cell is determined by using a probe liquid such as pentane to determine the "cell constant." The wicking rate of the pentane is used to determine the "cell constant". A Kruss

tensiometer can be used to determine this wicking rate. Based on this “cell constant,” the contact angle of the pentane is assumed to be zero and the liquid is non-interacting with the filler surface. The cell constant is calculated according to equation (1):

$$C = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma} \quad (1)$$

wherein:

| | |
|-------------------------------|---------------------------------------|
| m = Mass of liquid imbibed | ρ = Density of pentane |
| t = Time of wicking | γ = Surface tension of Pentane |
| η = Viscosity of Pentane | C = Cell Constant |

[0027] Once the cell constant is determined, it can be used to determine the contact angles of the subsequent filler with the probe liquids. This data can then be used to plot a linear relationship that exists between the square of the mass and the time. A slope can be used to calculate the contact angle based on the pentane “cell constant” according to equation (2):

$$\cos(\theta) = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma C} \quad (2)$$

wherein:

| | |
|--------------------|--------------------------------------|
| m = Mass | ρ = Density of liquid |
| t = Time | γ = Surface tension of liquid |
| η = Viscosity | C = Cell Constant |

[0028] Once the contact angle of the filler or fillers is measured with a series of probe liquids, the contact angles determined from each liquid can be used to determine the surface energy components for each filler. The surface energy is calculated from the measured contact angles according to equation (3), where S (solid) refers to the filler and L (liquid) refers to the matrix:

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^\delta \gamma_L^\delta)^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_S^- \gamma_L^+)^{1/2} \quad (3)$$

wherein:

| | |
|--------------------------|----------------------------|
| θ = Contact Angle | γ^+ = Lewis Acidity |
|--------------------------|----------------------------|

γ^{δ} = Dispersive Component γ^{-} = Lewis Basicity

γ_L = Surface tension of the liquid

[0029] As can be seen above, the determination of the solid properties requires solving a system of three equations and three unknowns. The first step in the calculation involves a substitution of the contact angle for the filler for at least one probe liquid in the equation. This initial substitution determines the dispersive component of the filler. When the probe liquid used, for instance, has an acid and base component of zero, the calculation described above is quite possible. Thus, at least one probe liquid that has an acid and base component of zero is preferred, such as bromonaphthalene. With using such a probe liquid, the dispersive component of the solid is fixed and the other components of the surface free energy are calculated from the remaining contact angles and liquid property data substituted into equation (3).

[0030] As part of the method of the present invention, the contact angle of the fluid matrix on a solid is also obtained. Preferably, the contact angle of the matrix is based on at least three different solids, such as, but not limited to, polyethylene, polyvinylchloride, and polymethylmethacrylate. Preferably, at least one of these probe solids has an acid constant and a base constant of zero in order to easily determine the other variables in the contact angle equation, as discussed above for the filler.

[0031] Once the contact angles of the matrix, based on preferably at least three probe solids, is known, the surface energy components of the matrix can be determined. Once the surface energy components of the matrix are determined as well as the surface energy components of the filler, the work of adhesion of matrix to the filler and the work of cohesion of the filler can be determined. The difference between the work of cohesion and the work of adhesion can be determined, which can then be correlated to a particular rheological property, such as yield point, of the composition comprising the filler in the matrix.

[0032] In more detail, as part of the present invention, a rheological property of the composition is determined. Any rheological property of a matrix which is effected by the presence of a filler can be measured, such as, for example, the yield point (also known as Bingham yield), the viscosity at a defined shear rate, or the ratio of the change in viscosity to the change in shear rate. Other rheological properties will be known to one skilled in the art.

By doing this actual measurement of the rheological property and comparing it to the difference in the work of cohesion and the work of adhesion, a rheological master curve and/or master formula can be created. Examples of a rheological master curve are shown below (Figures 2 and 3) and provide an indicator or prediction with respect to a filler-containing system and the rheological property, such as yield point, that will result. Thus, one knowing the difference in the work of cohesion and the work of adhesion for a particular composition comprising a filler in a matrix, one can immediately determine or predict the yield point that will be achieved by such a filler-matrix combination.

[0033] It is important to note that the rheological master curves apply to a particular filler loading, a particular morphology, and a particular temperature. For example, Figures 2 and 3 below are curves for a composition at a 10% filler loading. At other loadings or varying morphology (e.g., different DBPs), this rheological master curve and formula may shift to some extent based on the morphology of the filler and/or amount of loading in the matrix. Thus, various rheological master graphs or master formulas can be created depending on the loadings for various compositions and ultimately a third axis can be created to form a three-dimensional graph representing the effects of, for example, loading on the difference in the work of cohesion and the work of adhesion and yield point.

[0034] As shown in the rheological master curves below, once the difference in the work of adhesion and the work of cohesion are known for a particular composition, one can readily determine which filler to use in order to achieve the desirable yield point. Thus, in another embodiment, the present invention relates to a method of choosing a filler for a composition comprising a filler in a matrix. Knowing the desired yield point value, one could use the rheological master curve to determine the target difference between the work of cohesion of the desired filler and the work of adhesion of the matrix to the desired filler. Knowing or determining the surface energy components for the matrix will allow one to determine the surface energy components for the desired filler. This can be done, for example, by measuring the rheological properties of compositions containing various probe fillers, in which the surface energy properties of the probe fillers are known or measured (for example, using the methods described herein). Using the rheological master curve, the differences between the work of cohesion of each probe filler and the work of adhesion of the matrix to the probe filler can be obtained. Using the surface energy properties of the probe fillers, in

combination with the correlated difference, one can calculate the surface energy components for the matrix. Now, having these values, and combining these with the desired rheological properties of the specific composition, one can determine what surface energy properties the target filler must have in order to achieve this property. Further, if a library of this data is kept, a particular filler can be immediately provided to obtain the desired rheological property. Alternatively, if such a filler is not available, a process could be developed for preparing the target filler having the desired surface energy components. Essentially, in one embodiment of the present application, the surface energies of the filler can be dialed in to ultimately form the desired yield point and other rheological properties of the polymer composition, which can be important in various applications of the composition in a variety of industries. For example, if one desires a composition having a high yield point, which is beneficial in such applications as adhesives and sealants, a filler would be chosen which gives a difference between the work of cohesion and the work of adhesion that is also relatively high. This is a direct result of the rheological master curves of the present invention and produced by the method of the present.

[0035] Accordingly, the rheological master curve and formula applies to all types of fillers and matrices and is quite useful once the difference in the work of cohesion and the work of adhesion are known. The ability to accurately predict the rheological properties (for example, yield point or stress) of a filler-containing composition as well as the ability to choose a filler to achieve a desired rheological property without the need for time consuming and expensive iterative evaluations thus provides one skilled in the art the ability to control the rheological properties of the composition. Thus, in another embodiment, the present invention relates to the ability to control and/or predict rheological properties based on the above-described procedure(s). Furthermore, the present application relates to compositions or systems comprising at least one filler in a matrix that are formed based on the methodology described above as well as the use of the rheological master curve and/or master formula.

[0036] The above-described embodiments of the present invention can be incorporated into computer programs and/or software to run the above-described methodologies. Also, in another embodiment, the above-described embodiments, can even be provided on the internet, for instance, through a website that permits end users to determine or find the appropriate filler for their matrix, or vice versa, in order to achieve certain desired rheological properties.

[0037] The present invention will be further clarified by the following examples, which are intended to be exemplary of the present invention.

EXAMPLES

Example 1

[0038] To show the determination of the master curve which correlates the difference between the work of cohesion and the work of adhesion to yield points, the following experiment was conducted. In addition, this experiment was also conducted in order to show the predictive value of the present invention as well as the ability of the present invention to determine yield points of various fillers.

[0039] The following describes a method for determining the wicking rates of various liquids into porous powder beds of carbon black particles. The wicking rates are subsequently used to calculate the contact angles of a probe liquid with a given carbon black surface. In turn, the surface free energy components of the carbon black are estimated from the contact angles by the van Oss approach.

[0040] The wicking rates of the liquids listed in Table 1 with various carbon black powders were measured using a Kruss K12 Tensimeter. The technique involved packing a FL-12 Kruss powder cell with the carbon black (or other filler). A single run involved the following:

Table 1. Properties of various probe liquids

| Liquid | Viscosity (mPas) | Surface Tension (mN/m) | Density (g/ml) | γ_d (mN/m) | γ^+ (mN/m) | γ^- (mN/m) |
|-------------------------|------------------|------------------------|----------------|-------------------|-------------------|-------------------|
| Pentane | 0.24 | 15.5 | 0.629 | 15.5 | 0 | 0 |
| Water | 1 | 72.8 | 0.998 | 21.8 | 25.5 | 25.5 |
| Formamide | 3.81 | 58.2 | 1.133 | 39 | 2.28 | 39.6 |
| Ethylene Glycol | 21.81 | 48.3 | 1.109 | 29 | 1.92 | 47 |
| Bromonaphthalene | 5.11 | 44.6 | 1.483 | 44.4 | 0 | 0 |
| Tetrahydrofuran | 0.461 | 26.4 | 0.8844 | 27.4 | 0 | 15 |
| Diodomethane | 2.76 | 50.8 | 3.325 | 50.8 | 0 | 0 |
| Methyl Sulfoxide (DMSO) | 2 | 44 | 1.101 | 36 | 0.5 | 32 |

[0041] An FL-12-PLP filter was placed into the bottom of the cell prior to the addition of 0.5-1.0 grams of carbon black powder. This prevented the powder from escaping from the bottom of the cell. The cap, which was equipped with a Teflon piston attached to a threaded shaft, was screwed to the top of the cell. The piston was then advanced by turning the plunger

shaft until the bed was packed sufficiently. Typically, the number of shaft rotations were counted to consistently compress a given carbon black sample.

[0042] The packed powder cell was then placed on the K-12 tensiometer microbalance. The wicking rate of the pentane was used to determine the “cell constant”. It was assumed that the contact angle of the pentane was zero and the liquid was non-interacting with the carbon black surface. The cell constant was calculated according to equation (1):

$$C = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma} \quad (1)$$

wherein:

| | |
|-------------------------------|---------------------------------------|
| m = Mass of liquid imbibed | ρ = Density of pentane |
| t = Time of wicking | γ = Surface tension of Pentane |
| η = Viscosity of Pentane | C = Cell Constant |

The cell constant was recorded and was used to determine the contact angles with subsequent probe liquids as listed in Table 1.

[0043] After each run, the cell was thoroughly cleaned. The carbon black and solvent was removed from the cell and discarded. The cell was then rinsed with acetone and was sonically cleaned in hexane. The cell was dried with a lint free cloth and further dried with compressed nitrogen.

[0044] In order to form the rheological master curve or formula, a correlation was determined between the surface energies of various fillers and the yield point that resulted from the composition containing the filler. The rheological master curve was created based on the data set forth in Table 2 below:

Table 2: Surface energy components of the selected carbon black samples

| Sample | γ^d (mN/m) | γ^+ (mN/m) | γ^- (mN/m) |
|----------------|-------------------|-------------------|-------------------|
| Carbon Black A | 21.1 | 5.20 | 0.45 |
| Carbon Black B | 19.00 | 12.4 | 0 |
| Carbon Black C | 34 | 5.9 | 0 |

Determination of Yield Points

[0045] Yield points were determined using the following procedure. Ten (10) wt percent black was mixed with in each of the follow: Ethylene glycol, dimethyl sulfoxide, mineral oil, polydimethyl siloxane. Each mixture was placed in a “midgit mill” containing small shot. The mill was placed on a paint shaker and mixed for 30 minutes. The samples were filtered using a paint strainer to remove the shot. The samples were then tested on a Carri-Med rheometer for yield evaluation. Figure 1 gives typical results of the measured stress – strain plot obtained from the rheometer. The yield points determined in this way were plotted against the (Work of cohesion- Work of adhesion) determined as shown in more detail below.

Analysis of Data

[0046] A Kruss Tensiometer was attached to a computer that records the raw data file. The data was recorded as the mass of imbibed liquid as a function of time. It was determined that a linear relationship existed between the mass squared and time. The data was analyzed over the most linear region of the curve. The slope was used to calculate the contact angle based on the pentane “cell constant” according to equation (2):

$$\cos(\theta) = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma C} \quad (2)$$

wherein:

| | |
|--------------------|--------------------------------------|
| m = Mass | ρ = Density of liquid |
| t = Time | γ = Surface tension of liquid |
| η = Viscosity | C = Cell Constant |

Calculation of surface energy from contact angles

[0047] Carbon black samples were measured with a series of probe liquids as described above. The contact angles determined from each liquid were then used to calculate the surface energy components for each carbon black. The surface energy was calculated from the measured contact angles according to the van Oss/Good approach

equation (3). In order to solve for the three components (Dispersive, Acid, and Base) at least three probe liquids were used.

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^+\gamma_L^-)^{1/2} + 2(\gamma_L^+\gamma_S^-)^{1/2} \quad (3)$$

wherein:

θ = Contact Angle γ^+ = Lewis Acidity
 γ^d = Dispersive Component γ^- = Lewis Basicity
 γ_L = Surface tension of the liquid

[0048] The determination of the solid properties involved solving a system of three equations for three unknowns. The first step in the calculation involved the substitution of the contact angle for the carbon black/bromonaphthalene experiment (and the properties of bromonaphthalene) into the van Oss/Good equation. This initial substitution determined the dispersive component of the carbon black. This calculation was possible because the Acid and Base components of Bromonaphthalene are both zero. The now known dispersive component of the solid was fixed. The other components of the surface free energy were then calculated from remaining contact angle and liquid property data substituted into equation (3).

[0049] The second part of the experiment was to characterize the matrix. Several approaches could be taken, which are described in more detail below.

Method A

[0050] The properties of the fluid matrix were determined from the contact angle of the fluid on three different solids, *e.g.* polyethylene, polyvinylchloride, and polymethylmethacrylate. From these three contact angles, the characteristic surface tension components for the matrix were determined by the method of van Oss and Good as follows. (van Oss, C.J. "Interfacial forces in aqueous media"; Marcel Dekker: New York; 1994, incorporated in its entirety by reference herein).

[0051] The three contact angles can be measured by any appropriate technique, such as Morrison, I.D.; Ross, S. "Colloidal Dispersions"; John Wiley & Sons: New York; 2002, pp. 208 – 214, incorporated in its entirety by reference herein. The surface tension of the

fluid matrix can be measured by any appropriate technique such as Morrison, pp. 200 – 208, incorporated by reference herein.

[0052] The relation between the measured contact angle, θ , and measured surface tension of the fluid matrix, γ_L , on a given solid is given by equation (4) (van Oss, C.J. p. 22, equation III-13):

$$(1 + \cos\theta)\gamma_L = 2\left(\sqrt{\gamma_s^\delta\gamma_L^\delta} + \sqrt{\gamma_s^+\gamma_L^-} + \sqrt{\gamma_s^-\gamma_L^+}\right) \quad (4)$$

[0053] The known surface energy components for the three solids is given in Table 3 below:

Table 3: Surface tension components for standard polymers, at 20°C in mN/m

| Polymer | Dispersion constant γ_s^δ | Acid constant γ_s^+ | Base constant γ_s^- |
|----------------------------------|--|-------------------------------|-------------------------------|
| Polyethylene | 33.0 | 0 | 0 |
| Polymethylmethacrylate (PMMA) | 40.0 | 0 | 14.6 |
| Polyvinylchloride | 43.0 | 0.04 | 3.5 |

[0054] The three unknowns are the three components of the surface energy of the matrix. By measuring three contact angles, all three unknowns can be determined and the fluid matrix characterized.

Method B

[0055] Alternatively, the properties of the fluid matrix can be estimated by choosing a polymer to which it best corresponds. Table 4 shows various polymers and their surface tension components (from van Oss, p. 16.). The important correspondence is its Lewis acid

or Lewis base strength. (See Jensen, W.B. "The Lewis acid-base concepts"; John Wiley & Sons: New York; 1980 for an explanation of the key ideas, incorporated in its entirety by reference herein.) Further approximations can be made by using an appropriate average of similar polymers.

Table 4: Surface tension components of various synthetic polymers, at 20°C in *mN/m*

| Polymer | Dispersive | Acid | Base |
|-------------------------------|------------|------|------|
| Teflon FEP | 17.0 | 0 | 0 |
| Nylon 6.6 | 36.4 | 0.02 | 21.6 |
| Polyisobutylene | 25 | 0 | 0 |
| Polypropylene | 25.7 | 0 | 0 |
| Corn-treated polypropylene | 33.0 | 0 | 11.1 |
| Polyethylene | 33.0 | 0 | 0 |
| Polymethylmethacrylate (PMMA) | 40.0 | 0 | 14.6 |
| Polystyrene | 42 | 0 | 1.1 |
| Polyvinylpyrrolidone | 43.4 | 0 | 29.7 |
| Polyvinylchloride | 43.0 | 0.04 | 3.5 |
| Polyethyleneoxide | 43 | 0 | 64 |

Method C

[0056] Also, the properties of the fluid matrix can be estimated by choosing a liquid to which the fluid matrix best corresponds. The correspondence depends on the chemical nature, not the molecular weight of the matrix. The important chemical nature is taken to be the Lewis acid or Lewis base strength of the matrix. (See Jensen, W.B. "The Lewis acid-base concepts"; John Wiley & Sons: New York; 1980 for an explanation of the key ideas.) Values of the dispersion, acid, and base components of various common solvents are given in van Oss, pp. 172 – 173, incorporated in its entirety by reference herein.

Method D

[0057] Alternative methods to characterize the fluid matrix can also be used. Some of these are referred to in a review of the subject, Clint, J.H. "Adhesion and components of

solid surface energies.” Current Opinion in Colloid & Interface Science, 2001, 6, 28 – 33 and in the book, Berg, J.C., Ed. “Wettability” Marcel Dekker: New York; 1993, incorporated in its entirety by reference herein.

Method E

[0058] Another way to characterize the fluid matrix is to measure its wicking time on powders of known composition. The wicking of a liquid up a bed of packed powder is a method to determine the contact angle of a liquid on a solid (the Washburn method). The relation between the rate of wicking, L/t^2 , and the contact angle of a liquid of known surface tension, σ_{matrix} , and viscosity, η is given by equation (5):

$$\frac{L^2}{t} = \frac{r}{2\eta} \sigma_{matrix} \cos \theta \quad (5)$$

wherein r is found the usual way by measuring the wicking rate of a hydrocarbon liquid (equation (6)):

$$r = \frac{2\eta_{hc}}{\sigma_{hc}} \frac{L^2}{t_{hc}} \quad (6)$$

[0059] The figure above shows the relation between the thermodynamic quantity, $W^{coh} - W^{adh}$ and the yield point. The work of cohesion is just twice the surface tension of the solid (equation (7)):

$$W^{coh} = 2\sigma_{solid} \quad (7)$$

The work of adhesion is given by equation (8):

$$W^{adh} = \sigma_{liquid} (1 + \cos \theta) = \frac{2\eta}{r} \frac{L^2}{t} + \sigma_{liquid} \quad (8)$$

Therefore, as shown in equation (9):

$$W^{adh} - W^{coh} = \frac{2\eta}{r} \frac{L^2}{t} + \sigma_{liquid} - 2\sigma_{solid} \quad (9)$$

[0060] Considering this equation between wicking rates and the thermodynamics of particle structure in liquids and the relation between the thermodynamic function and yield points shown in the graph shows that wicking rates and yield points are related.

Calculation of Work of Adhesion and Work of Cohesion.

[0061] The work of adhesion between a solvent or a polymer of interest and the carbon black is calculated using the equation (10).

$$W^{adh} = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_L^+ \gamma_S^-)^{1/2} \quad (10)$$

The surface free energy components are known for the given carbon black and polymer. Thus the free energy of interaction can be quantitatively determined. Likewise the work of cohesion is calculated by using equation (11) and equation (12).

$$W_S^{coh} = 2\gamma_S^d + 2(\gamma_S^+ \gamma_S^-)^{1/2} \quad (11)$$

$$W_L^{coh} = 2\gamma_L \quad (12)$$

[0062] Figure 3 is a master curve illustrating ranges, within the upper and lower lines, of work of cohesion minus work of adhesion for a particular yield point.

Example 2

[0063] To show the determination of the rheological master curve which correlates the difference between the work of cohesion and work of adhesion and yield points in a single liquid at higher filler weight content than Example 1, the following experiment was conducted. In addition, the experiment illustrates the predictive value of the present invention as well as the ability of the present invention to determine yield points of various fillers using a single liquid and high weight percent filler. The method of determining the

wicking rates of various liquids into porous powder beds of carbon black particles was the same as that describe in Example 1.

[0064] In order to form the rheological master curve or formula, a correlation was determined between the surface energies of various fillers and the yield point that resulted from the composition containing the filler. The rheological master curve was created based on the data set forth in Table 5 below:

Table 5: Surface Energy Components of Selected Carbon Black Samples

| Sample | γ^d (mN/m) | γ^+ (mN/m) | γ^- (mN/m) |
|----------------|-------------------|-------------------|-------------------|
| Carbon Black E | 14.8 | 35.2 | 8.8 |
| Carbon Black F | 14.3 | 39.5 | 9.3 |
| Carbon Black G | 14.2 | 32.7 | 13.5 |
| Carbon Black H | 19.8 | 38.8 | 7.9 |
| Carbon Black I | 39.3 | 3.13 | 14.5 |
| Carbon Black J | 17.6 | 28.5 | 14.2 |

Determination of Yield Points

Yield points were determined using the following procedure. Fifteen (15) wt percent black was mixed with Ethylene Glycol. The mixture was placed in a “midgit mill” containing small shot. The mill was placed on a paint shaker and mixed upto 30 minutes. The samples were separated from the shot and subsequently tested for yield point on a Carri-Med rheometer in a similar manner described in Example 1.

[0065] The analysis of the data was performed similar to that described in Example 1. Results are shown in Figure 4 below, which is a rheological master curve relating yield point to the difference between the work of cohesion and the work of adhesion for a single fluid.

[0066] As can be seen, the present invention has the ability to predict quite effectively the yield points of a polymer-filler system. Furthermore, with the creation of the master curve, once one knows the work of adhesion and the work of cohesion, one can immediately predict the yield point of a filler in a polymer system.

[0067] Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as

exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.